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SELECTED THERMAL ANALYSIS TECHNIQUES AND APPLICATIONS

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ABSTRACT

Thermal analysis is regarded as one of the most useful and fastest growing analytical techniques in recent years. The purpose of this introductory report is to aquaint engineers and scientists, particularly those working in CANMET, with the capabilities and wide applications of the various thermal analysis techniques with special emphasis on the extremely useful techniques of thermogravimetry and differential thermal analysis.

TECHNIQUES ET APPLICATIONS D'ANALYSE THERMIQUE CHOISIES

par

S.A. Mikhail

RÉSUMÉ

Au cours de ces dernières années, l'analyse thermique est considérée comme l'une des méthodes d'analyse la plus utile et la plus rapide à se développer. L'objectif de ce rapport préliminaire est de présenter aux ingénieurs et scientifiques, surtout à ceux qui travaillent au CANMET, les capacités et les applications de grande portée des diverses méthodes d'analyse thermique tout en soulignant les techniques extrêmement utiles de la thermogravimétrie et de l'analyse thermique différentielle.

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According to the International Confederation for Thermal Analysis (ICTA), thermal analysis is a group of techniques in which some physical property of a substance and/or its reaction product(s) is measured as a function of temperature while the substance is subjected to a controlled temperature program. In some cases, such as isothermal thermogravimetry, measurements are done as a function of time. Various physical properties, Table 1, including mass, temperature, enthalpy, dimensions, etc., may be measured by thermal analysis.

Table 1. Classification of thermal analysis techniques[1].

Measured property	Principal techniques
Mass	Thermogravimetry (TG) Isobaric mass-change determination Evolved gas detection (EGD) Evolved gas analysis (EGA) Emanation thermal analysis (ETA)
Temperature	Heating curve determination Differential thermal analysis (DTA)
Enthalpy	Differential scanning calorimetry (DSC)
Dimensions	Thermodilatometry
Mechanical characteristics	Thermomechanical analysis (TMA) Dynamic thermomechanometry
Acoustic characteristics	Thermosonimetry Thermoacoustimetry
Optical characteristics	Thermoptometry
Electrical characteristics	Thermoelectrometry
Magnetic characteristics	Thermomagnetometry

An illustration of thermal analysis techniques as classified by ICTA is shown in Figure 1, where the thermal analysis technique is given in the outer circle, while the inner circle defines the measured physical property.

Figure 1: ICTA classification of TA techniques[1].

A survey of the two leading thermal analysis journals, namely, Thermochemica Acta (TCA) and the Journal of Thermal Analysis (JTA), is presented in Table 2. Thermal analysis techniques involving mass (thermogravimetry), temperature (differential thermal analysis) and enthalpy changes (differential scanning calorimetry) were found to be the most widely used ones. The first two techniques account for over 45% of the published experimental data on thermal analysis.

Table 2. Techniques used in thermal analysis[1].

	Percentage	
	TCA	JTA
1. TG (thermogravimetry)	29.1	22.0
2. DTA (differential thermal analysis)	16.7	26.2
3. DSC (differential scanning calorimetry)	6.8	6.8
4. DTG (derivative thermogravimetry)	6.2	4.5
5. X-ray, H.T.	4.6	4.2
6. MS (MTA) (mass spectrometry)	2.8	1.1
7. Elec. properties	2.2	1.4
8. EGD-EGA (evolved gas detection-analysis)	1.9	3.1
9. TMA (dilatometry)	1.9	1.1
10. Derivatography	1	13.2
11. Miscellaneous TA	18.5	13.3
12. Calorimetry, all types other than DSC	8.7	2.8
13. Total Number of papers in survey	220	245

Thermogravimetry (TG)

Thermogravimetry can be defined as a technique in which the change in sample mass is recorded as a function of temperature (dynamic thermogravimetry) or time (isothermal thermogravimetry). While the basic components of thermogravimetry, the balance and the fire, have existed for thousands of years, it was only in this century that the two were coupled in what is called a thermobalance. The thermobalance is an apparatus used to detect and, if required, record the changes in the mass of a substance being heated or cooled, as a function of temperature or time or these of a substance maintained isothermally as a function of time. The word thermobalance was introduced into the science by Kotara Honda, a professor at Tohoku University in Japan, in 1915.[2] He designed and put into use the first thermobalance as shown in Figure 2.

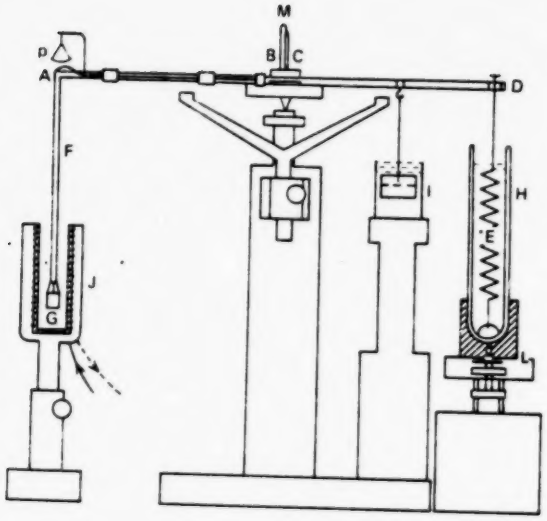

Figure 2. The thermobalance as described by Honda.[2]

It consisted of a balance with a quartz beam, with a porcelain tube F attached to one arm; this tube went down into an electrically heated furnace J and carried a porcelain dish G where the sample was placed. The other arm had a fine steel spring E immersed in oil contained in a Dewar flask H. Calibration was done by placing weights on the small pan P and, through an eye piece, maintianing the scale reading at zero by adjusting the position of the Dewar flask.

In 1923, Marcel Guichard, a professor of inorganic chemistry at the Sorbonne University in France built another thermobalance, Figure 3, in which a constant rate of heating was ensured by a gas burner fed via a constant level device R consisting of a valve with attached float. The water E, which supported the float, was fed slowly and regularly through a

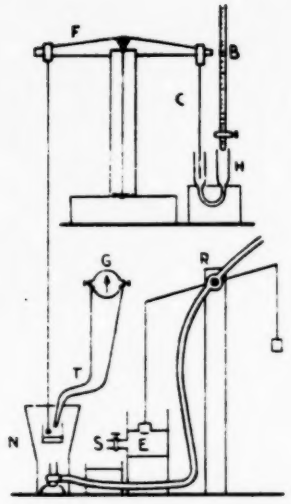

Figure 3. Diagram of the original Guichard thermobalance.[2]

sensitive valve S, thus causing slow and gradual opening of the valve R. The balance was compensated hydrostatically and the amounts of oil poured in were exactly proportional to the variations in the weights found if the balance was maintained at zero throughout. A loss in weight of 100 mg corresponded to an addition of 9 mL of oil. Later, Guichard substituted an electric furnace for the gas heating and replaced air by other gases, chosen especially for the experiments in mind.

Many other thermobalances were developed after Honda and Guichard and by 1961, more than fifty thermobalances were described in the literature and ten of those were commercially available. The advent of the modern automatic thermobalance began with the introduction of the electrobalance of Cahn and Schultz in 1963. Other commercial thermobalances followed such as Mettler, Dupont, Perkin-Elmer, Netzsch, ULVAC Riko, Stanton Redcroft and others. Today, the majority of modern equipment are microprocessor controlled with automatic recording devices.

A schematic diagram of a modern thermobalance is shown in Figure 4.

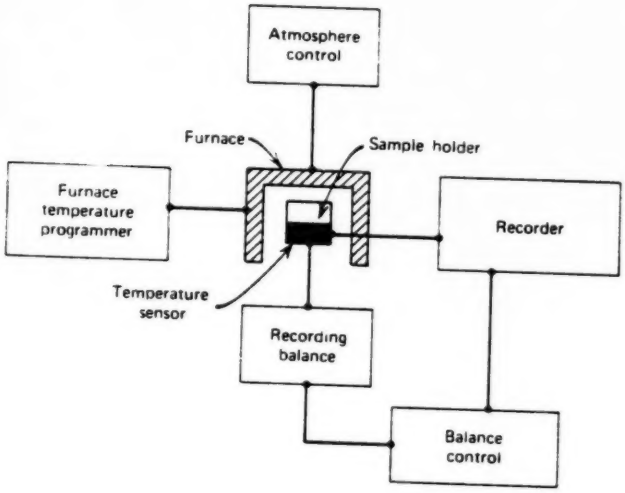

Figure 4. Schematic diagram of a modern thermobalance.[3]

It generally consists of a recording balance, a furnace, a furnace temperature programmer or controller and a strip chart or X-Y recorder. A modern data acquisition system may substitute for or be run in conjunction with the recorder. As shown in Figure 5, the furnace may be positioned above, below or parallel to the balance.

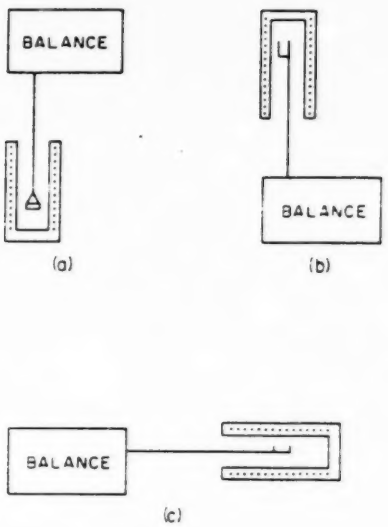

Figure 5. Furnace position in the thermobalances: (a) below balance; (b) above balance; (c) parallel to balance.[4]

A typical TG curve for a single stage reaction is illustrated in Figure 6 and for a multiple stage reaction in Figure 7.

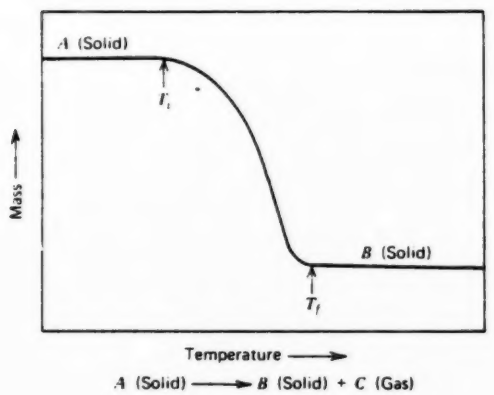

Figure 6. Characteristics of a single-stage reaction TG curve.[3]

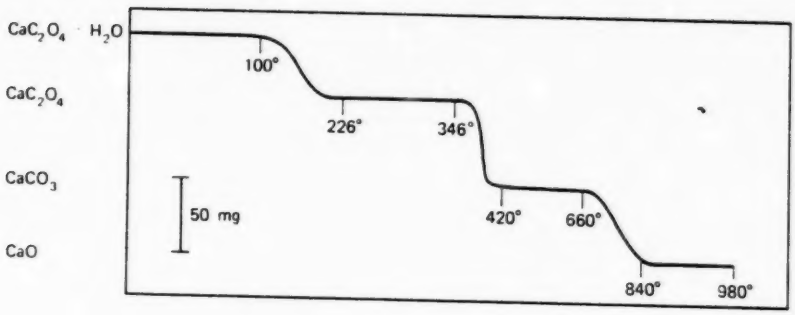

Figure 7. TG diagram of $CaC_2O_4.H_2O$ in dry N_2.[3]

The latter is the TG curve for calcium oxalate monohydrate. The first weight loss above 100°C indicates the dehydration. The second around 400°C is the decomposition of the oxalate releasing CO and the last between 660 and 840°C is the decomposition of the carbonate to the oxide.

The method of thermogravimetry is basically quantitative in nature and is widely used in the fields of metallurgy, fossil fuels, ceramics, mineralogy, catalysis, organic and inorganic chemistry, polymer chemistry, biochemistry, geochemistry and many other fields. Generally, the application of thermogravimetry to a particular problem is possible if a mass change is observed on the application of heat. Mass changes which can be detected by TG techniques may be summarized in Figure 8.

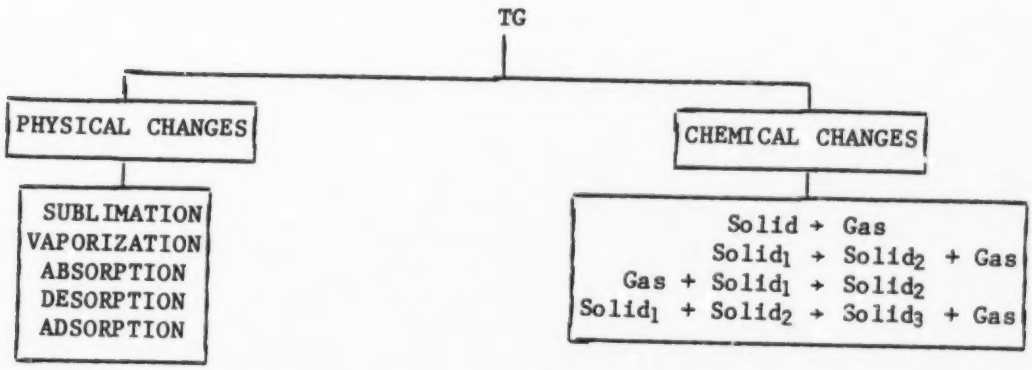

Figure 8. Mass changes detectable by TG.[3]

Some of the many applications of thermogravimetry are summarized in Table 3.

Table 3. Some applications of thermogravimetry.[4]

1.	Thermal decomposition of inorganic, organic and polymeric substances
2.	Corrosion of metals in various atmospheres at elevated temperatures
3.	Solid-state reactions
4.	Roasting and calcining of minerals
5.	Distillation and evaporation of liquids
6.	Pyrolysis of coal, petroleum and wood
7.	Determination of moisture, volatiles, and ash contents
8.	Rates of evaporation and sublimination
9.	Dehydration and hygroscopicity studies
10.	Phase diagrams and nonstoichiometry
11.	Thermal oxidative degradation of polymeric substances
12.	Decomposition of explosive materials
13.	Development of gravimetric analytical procedures
14.	Reaction kinetics studies
15.	Discovery of new chemical compounds
16.	Vapor pressure determination and heats of vaporization
17.	Adsorption, desorption curves
18.	Magnetic properties; e.g., Curie temperature, magnetic susceptibility

Differential thermal analysis (DTA)

Differential thermal analysis (DTA) is a thermal technique in which the temperature of the sample (T_s), compared with the temperature of a thermally inert material (T_r), is recorded as a function of the sample, inert material or furnace temperature during heating or cooling at a uniform rate. In DTA, the temperature changes as a result of chemical or physical changes in the sample are detected by a differential method as illustrated in Figure 9.

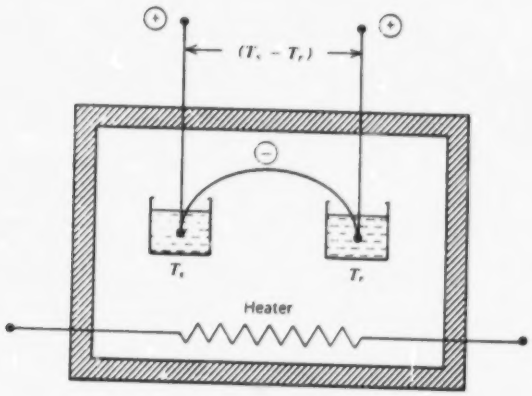

Figure 9. Basic DTA system.[3]

The changes in the sample temperature during heating or cooling take place due to endothermic or exothermic enthalpic transitions or reactions such as those caused by phase changes, fusion, boiling, sublimation, dehydration reactions, decomposition reactions, oxidation, reduction and other chemical reactions.

Accurate temperature measuring techniques, such as thermocouple, resistance thermometer and optical pyrometer were well established in Europe by the late 1800s and were soon used in the study of chemical systems at elevated temperatures. Le Chatelier in 1887, who was interested in both

clay mineralogy and pyrometry, introduced the use of heating-rate-change curves to identify clays. The differential temperature method was conceived by the metallurgist Roberts-Austen in 1889. The difference between the temperature of the sample (T_s) and that of the reference material (T_r) was observed directly on one galvanometer, whereas the sample temperature (T) was obtained on another. Saladin in 1904 developed a photographic recorder that recorded T_s-T_r versus T directly. A photographic recorder, which used a rotating drum, was developed by Kurnakov in 1904. This instrument was used extensively by Russian workers in DTA for 50 or 60 years. The modern era of DTA instrumentation began with the introduction of the dynamic gas atmosphere DTA system by Stone in 1951. This system permitted the flow of gas or vapour through the sample during heating or cooling cycles.

The 1960's saw the introduction of elaborate DTA instruments including the development of the differential scanning calorimetry and other notable systems by Mettler, DuPont, Deltatherm, Perkin-Elmer and others.

A schematic diagram of a typical DTA apparatus is shown in Figure 10.

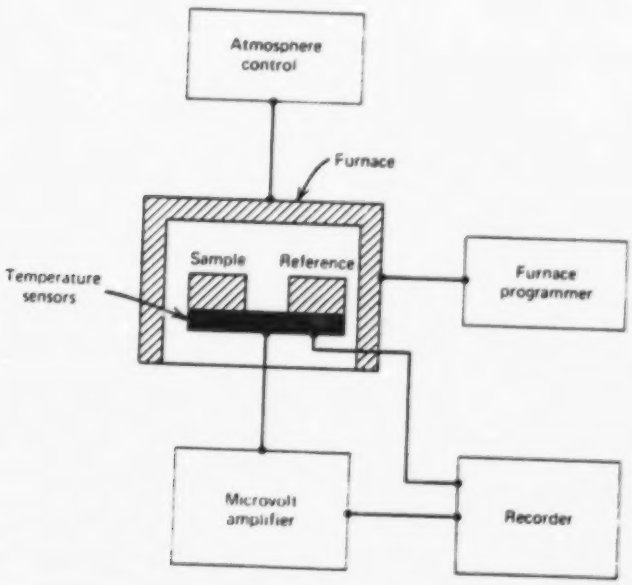

Figure 10. Schematic diagram of a typical DTA apparatus.[3]

The system generally consists of a furnace, a furnace temperature programmer, a sample and reference holder, a differential temperature detector, a DC amplifier, a recorder and control equipment for maintaining a suitable atmosphere in the furnace and sample holder.

A typical DTA curve is illustrated in Figure 11.

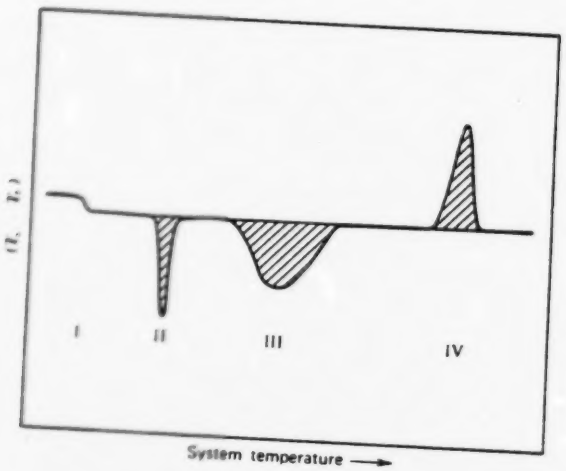

Figure 11. Typical DTA curve.[3]

The first base line deviation corresponds to a second order transition*, the second is an endothermic peak caused by fusion or melting, the third endothermic peak may be due to a decomposition reaction and the fourth exothermic peak may be due to an oxidation reaction, crystalline phase change and so on, not necessarily in the same order. Some of the phenomena that give rise to observable effects in DTA are given in Table 4.

*Second order transition may also appear as a peak e.g. Curie point transition.

Table 4. Physicochemical origin of DTA and DSC curve peaks.[3]

Phenomena	Enthalpic change (on heating)	
	Endothermal	Exothermal
Pysical		
Crystalline transition	X	X
Fusion	X	
Vaporization	X	
Sublimation	X	
Adsorption		X
Desorption	X	
Absorption	X	
Curie point transition	X	
Glass transition	Change of base line, no peaks	
Liquid crystal transition	X	
Heat capacity transition	Change of base line, no peaks	
Chemical		
Chemisorption		X
Desolvation	X	
Dehydration	X	
Decomposition	X	X
Oxidative degradation		X
Oxidation in gaseous atmosphere		X
Reduction in gaseous atmosphere	X	
Redox reactions	X	X
Solid-state reaction	X	X
Combustion		X
Polymerization		X
Pre-curing (resins)		X
Catalytic reactions		X

A DTA curve for calcium oxalate monohydrate in oxygen is shown in Figure 12.

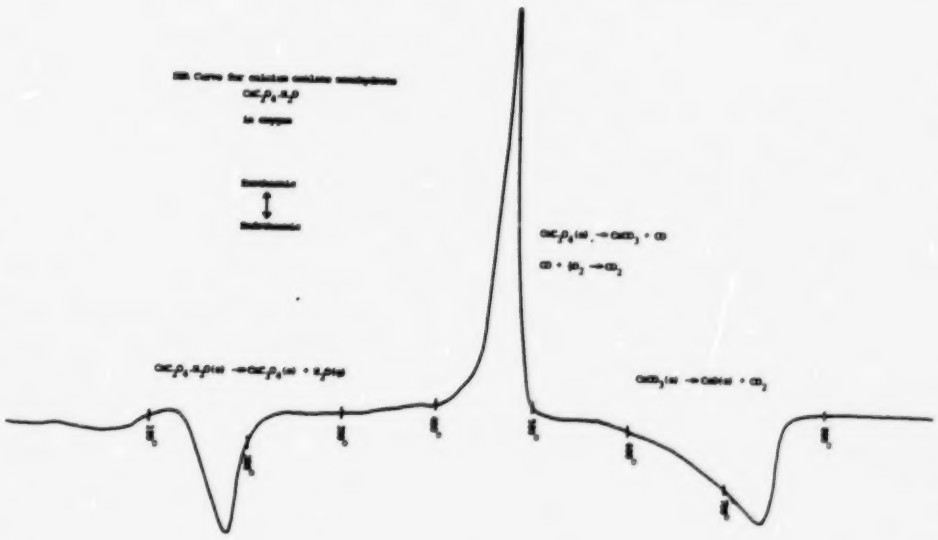

Figure 12. DTA diagram of $CaC_2O_4.H_2O$ in oxygen

The first endothermic peak indicates the dehydration of the oxalate. The second exothermic peak is the net result of 2 thermal effects; an endothermic decomposition of calcium oxalate to calcium carbonate and CO and an exothermic oxidation of CO to CO_2. The final endothermic peak indicates the decomposition of calcium carbonate to give the oxide. When the same compound is heated in an inert atmosphere instead of air, the oxidation of CO to CO_2 is suppressed and the DTA diagram would contain 3 endothermic peaks; for the dehydration, the decomposition of the oxalate to carbonate and the decomposition of the carbonate to the oxide.

The technique of DTA has been employed by geologists, ceramicists, metallurgists and recently by chemists in a large number of applications. Table 5 illustrates some of the applications of DTA and DSC in chemistry and shows a variety of materials and the types of studies that can be performed on them.

Table 5. Some applications of DTA and DSC.[4]

Catalysts	Decomposition reactions
Polymeric materials	Phase diagrams
Lubricating greases	Reaction kinetics
Fats and oils	Solid-state reactions
Coordination compounds	Dehydration reactions
Carbohydrates	Radiation damage
Amino acids and proteins	Heats of adsorption
Metal salt hydrates	Heats of reaction
Metal and nonmetal oxides	Heats of polymerization
Coal and lignite	Heats of sublimation
Wood and related substances	Desolvation reactions
Natural products	Solid-gas reactions
Clays and minerals	Curie point determinations
Metals and alloys	Purity determinations
Soil	Thermal stability
Biological materials	Oxidation stability
Amorphous materials	Glass transition determinations
Cements	Comparison
Semiconductors	Hazards evaluation
Pharmaceuticals	Thermal conductivity
Explosives	Specific heats

Some important industrial applications of DTA are also shown in Table 6.

Table 6. Important industrial applications of DTA.[5]

DTA is vital in the study of To determine or evaluate	Ceramics	Cements	Chemicals	Elastomers	Explosives	Forensic Chemistry	Fuels	Glass	Inks	Metals	Minerals	Paints	Pharmaceuticals	Phosphors	Plastics	Propellents	Soaps	Soils	Textiles
Identification	✓		✓	✓	✓	✓	✓		✓	✓	✓		✓	✓	✓	✓	✓	✓	✓
Composition (Quantitative)	✓	✓	✓	✓	✓	✓			✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
Phase Diagrams	✓	✓	✓					✓		✓	✓			✓	✓	✓	✓		
Solvent Retention			✓	✓	✓	✓			✓			✓	✓	✓	✓	✓	✓		✓
Hydration-Dehydration	✓		✓			✓					✓		✓	✓				✓	✓
Thermal Stability			✓	✓	✓		✓		✓		✓	✓	✓	✓	✓	✓	✓		✓
Oxidative Stability			✓	✓	✓		✓		✓	✓		✓	✓	✓	✓	✓	✓		✓
Polymerization				✓			✓		✓			✓			✓				
Curing				✓	✓	✓						✓			✓	✓			
Purity			✓			✓							✓				✓		
Reactivity		✓	✓					✓		✓	✓	✓	✓	✓	✓	✓	✓		
Catalytic Activity	✓	✓	✓				✓	✓		✓	✓								
Glass Transitions				✓	✓										✓	✓			✓
Radiation Effects	✓	✓				✓	✓	✓		✓	✓	✓		✓	✓	✓			✓
Thermochemical Constants	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓

A wide range of scientific disciplines have recognized thermal analysis as an important tool in acquiring information. The following titles of recent publications were selected to demonstrate the flexibility of thermal analysis techniques.

1. Applications of thermal analysis to the communications and electronics industry.
2. Thermogravimetric analysis as a means for following corrosion reactions in sealed systems.
3. Thermal investigation of electric insulating materials.
4. A study on the thermal behaviour of some explosives.
5. Coal, oil shale and thermal analysis.
6. Thermal analytical fossil fuel research.
7. Microcalorimetric studies of native human plasma protein sorption.
8. Thermal studies of proteins, peptides and aminoacids II. Thermogravimetry.
9. Thermal analysis in the pharmaceutical industry.
10. Thermoanalytical investigation of the action of flame retardants.
11. Thermoanalytical study on fertilizer components and their mixtures.
12. DSC study of unsaturated polyester resin stability.
13. Thermal analysis of mixtures of polyvinyl chloride and some coke and petrochemical products.
14. Thermal analysis in rubber industry.
15. Thermogravimetric analysis of thin silver films.
16. DTA as a significant means for the characterization of ceramic clays.
17. Thermal analysis as an aid to the criminalist.
18. The application of DTA, TG to trouble shooting of Portland cement burning process.
19. Thermoanalytical measurements in archaeometry.
20. Calorimetry of small animals and some consequences of the thermodynamics of irreversible processes.

In the Physical Chemistry Section at CANMET, thermal analysis has been used frequently as the principal technique in many studies[6] and often in problem solving and trouble shooting in many of CANMET's projects.

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POOR

QUALITY

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